PATENT ABSTRACTS OF JAPAN

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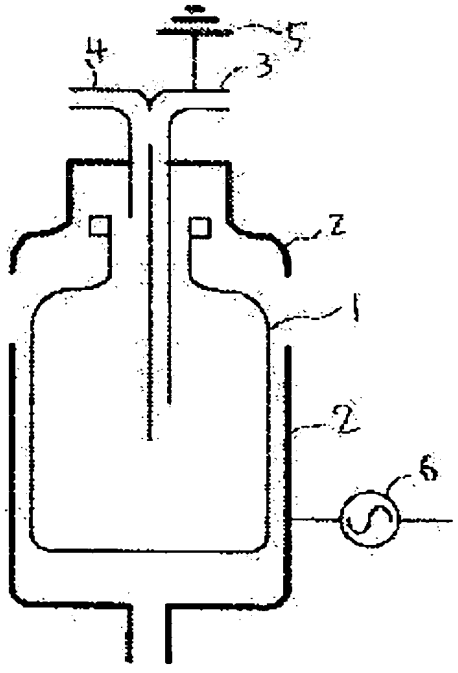
(54) PLASTIC CONTAINER AND MANUFACTURE THEREOF



(57)Abstract:

PROBLEM TO BE SOLVED: To improve the barrier property, transparency, impact-resistance and flexibility or the like by forming a barrier layer wherein the carbon content or the like is changed during one film forming by a plasma CVD method using a gas having a vaporized organic silicon compound, and a gas having an oxida tion function in a plasma or the like.

SOLUTION: By using a gas having at least an organic silicon compound and oxygen or a gas having an oxidation function, a barrier layer containing a silicon compound, and at least one kind of compound comprising one or more kinds of elements from among carbon, hydrogen, silicon and oxygen, is formed at least on one side of a plastic container by a plasma CVD method. For example, the plastic

container 1 is set in an external electrode 2, and a gas introducing pipe 3 which becomes a grounding 5, and an air discharging port 4 are set. Then, the inside and the outside of the plastic container 1 are vacuumized, and a required gas or the like is made to flow from the gas introducing pipe 3, and at the same time, a high frequency is applied to the external electrode 2, and a plasma is generated, and a film forming is performed on the internal surface of the plastic container 1.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the plastic envelope characterized by the concentration of an organosilicon compound changing in case the barrier layer which contains at least at least one kind of compound of a plastic envelope which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on one side by the plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least.

[Claim 2] The manufacture approach of the plastic envelope according to claim 1 characterized by decreasing while the concentration of an organosilicon compound forms membranes.

[Claim 3] The manufacture approach of the plastic envelope according to claim 1 characterized by repeating reduction and an increment while the concentration of an organosilicon compound forms membranes.

[Claim 4] The manufacture approach of the plastic envelope characterized by being in the middle of membrane formation, and stopping supply of an organosilicon compound in case the barrier layer containing at least one kind of compound which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on a base material by the plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least.

[Claim 5] The manufacture approach of the plastic envelope which is about supply of an organosilicon compound in the middle of membrane formation, and is characterized by the stop and starting supply again in case the barrier layer containing at least one kind of compound which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on a base material by the plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least.

[Claim 6] The manufacture approach of the plastic envelope characterized by being about supply of an organosilicon compound in the middle of membrane formation, and repeating a stop and starting supply again in case the barrier layer containing at least one kind of compound which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on a base material by the plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least.

[Claim 7] The manufacture approach of the plastic envelope characterized by both

the flow rates of the gas which has the flow rate and the oxygen, or the oxidizing power of an organosilicon compound in case the barrier layer containing at least one kind of compound which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on a base material by the plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least changing.

[Claim 8] The manufacture approach of the plastic envelope characterized by preparing which barrier layer of claims 1-7 in a bottle inner surface.

[Claim 9] The plastic envelope characterized by having the plasma-CVD barrier layer in which the concentration containing at least one kind of compound which consists of at least one sort or two sorts or more of elements of an organosilicon compound changes out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on one side at least.

[Claim 10] The plastic envelope according to claim 9 characterized by decreasing while the concentration of an organosilicon compound forms membranes.

[Claim 11] The plastic envelope according to claim 9 characterized by repeating reduction and an increment while the concentration of an organosilicon compound forms membranes.

[Claim 12] The plastic envelope according to claim 9 characterized by both the concentration and oxygen densities of an organosilicon compound changing in the thickness direction.

[Claim 13] The plastic envelope characterized by preparing which barrier layer of claims 9-12 in a bottle inner surface.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a gas barrier nature plastic envelope and a container excellent in gas barrier nature, transparency, and pair impact nature with respect to the manufacture approach of a plastic envelope of having prepared the gas barrier film.

[0002]

[Description of the Prior Art] Generally, the plastic envelope is widely used as a container in the field with the various food fields, drugs fields, etc. from various

properties, such as the ease of the shaping, and lightweight nature, a point which is low cost further.

[0003] However, since plastics has the property which penetrates low-molecular gas like oxygen, a carbon dioxide, and a steam and has the property in which a low-molecular organic compound will stick to the interior further as known well, a plastic envelope receives constraint with the various activity gestalten for an activity compared with other containers, such as glass.

[0004] For example, since the drink which is contents will cause oxidization with time, and will deteriorate, and the carbon dioxide gas of a carbonated drink will penetrate plastics and will be emitted to the exterior of a container by the oxygen which penetrates plastics and permeates the interior of a container when a plastic envelope is filled up with carbonated drinks, such as Biel, a carbonated drink will turn into a drink from which mind escaped.

[0005] Moreover, since plastics is adsorbed in the aroma components (for example, limonene of orange juice etc.) which are the low-molecular organic compounds contained in a drink when a plastic envelope is filled up with the drink which has aroma components, such as orange juice, the presentation of the aroma component of a drink loses balance and there is a possibility that the quality of a drink may deteriorate.

[0006] Furthermore, also in case powder, such as instant coffee, is saved in a plastic envelope, there is a possibility that the quality of contents may deteriorate, with the steam which penetrated plastics and permeated the interior of a container.

[0007] Moreover, about a plastic envelope, elution of the low molecular weight compound contained during the presentation may become a problem. That is, when filled up with the contents (especially liquid) as which purity is required of a plastic envelope, the plasticizer contained during the plastics presentation, and a residual monomer and other additives may be eluted in contents, and may spoil purity of contents.

[0008] On the other hand, although recovery of a used container has social-problem-ized now and recycle-ization of a resource is advanced, even if it is going to use a plastic envelope as a re-restoration container, if it is left in the environment to recovery after the activity unlike the case of glassware, various low-molecular organic compounds, such as a mold odor, will stick to a plastic envelope between them.

[0009] As for this low-molecular organic compound to which it stuck, after washing remains in plastics. For this reason, when a plastic envelope is used as a re-restoration container, the low-molecular organic compound to which it stuck

begins to melt gradually into the contents with which it filled up as heterogeneity, and the debasement of contents and a sanitary problem arise.

[0010] For this reason, there is almost no example for which the plastic envelope is used as a returnable container.

[0011] In order to control the property in which the property and low-molecular organic compound which penetrate the low-molecular gas of the above plastic envelopes will stick to the interior Although orientation of the plastics is carried out, crystallinity is raised or the approach of carrying out the laminating of adsorbent low plastics, the thin film of aluminum, etc. more is also used Neither gas barrier nature nor the problem of adsorption can be solved thoroughly, with the special feature of a plastic envelope maintained that all are called transparency and easy disposability.

[0012] Although the technique of using a plasma-CVD method for a plastic envelope in recent years, and performing coating here is known, since it is ineffective to the problem of the low-molecular organic compound which sticks to a container inner surface by the approach of forming membranes on the outside surface of a bottle, it is desirable to form membranes especially to the inner surface of a bottle.

[0013] What is depended on the DLC film as an example of coating in the plasma-CVD method to a bottle inner surface is reported (JP,8-53117,A). It is amorphous carbon which made the subject SP [between carbon]3, and SP2 association, and this DLC film is dramatically hard and is hard carbon film which has very smooth mol FOROJI with a high refractive index.

[0014] What is furthermore depended on the silicon oxide film as an example of inner surface coating of a plastic envelope is reported. (JP,8-175528,A) Making it the two-layer structure of the organic polymerization film and the silicon oxide film is also described by this example.

[0015] Then, we have already reported the object by the film containing the compound which consists of at least one sort or two sorts or more of elements out of silicon oxide, carbon, hydrogen and silicon, and oxygen as an example of coating of a plastic envelope, in order to conquer the problem of flexibility which poses a problem by the transparency which poses a problem by the DLC film, and the silicon oxide film. (Japanese Patent Application No. 10-186393)

[0016]

[Problem(s) to be Solved by the Invention]

[0017] However, although supplying a raw material to a large quantity and exhausting to a large quantity is called for by the plasma-CVD method, much cost is needed for strengthening an exhaust air system.

[0018] Although there is also the approach of dividing material gas into an organosilicon compound and oxygen, and supplying it, now, the increment in membrane formation time amount is imitated, and there is a fault of **.

[0019] This invention is made in view of such a situation, and aims at offering the manufacture approach of a gas barrier nature plastic envelope excellent in barrier nature, transparency, pair impact nature, and flexibility.

[0020]

[Means for Solving the Problem]

[0021] In order to attain such an object, the manufacture approach of the gas barrier nature plastic envelope of this invention and a container are the objects aiming at the burden to an exhaust air system, and reduction of membrane formation time amount by changing the gas concentration under membrane formation.

[0022] Namely, the manufacture approach of the gas barrier plastic envelope by this invention By ** for gas and the plasma-CVD method for having oxidizing power in the gas which has the organosilicon compound made to evaporate, oxygen, or the plasma, to a plastic envelope A silicon oxide, It is the object which forms the barrier layer which changed the carbon content in the film etc. during one membrane formation by forming the film which contains the compound which consists of at least one sort or two sorts or more of elements out of carbon, hydrogen, silicon, and oxygen, and changing gas concentration.

[0023] Even if there are specifically few plastic envelopes, in invention of claim 1, on one side by the plasma-CVD method using the gas which has an organosilicon compound, oxygen, or oxidizing power at least A silicon oxide, In case the barrier layer which contains at least one kind of compound which consists of at least one sort or two sorts or more of elements out of carbon, hydrogen, silicon, and oxygen is formed, the manufacture approach of the plastic envelope characterized by the concentration of an organosilicon compound changing is offered.

[0024] In invention of claim 2, the manufacture approach of the plastic envelope according to claim 1 characterized by decreasing while the concentration of an organosilicon compound forms membranes is offered.

[0025] In invention of claim 3, while the concentration of an organosilicon compound forms membranes, the manufacture approach of the plastic envelope according to claim 1 characterized by repeating reduction and an increment is offered.

[0026] In invention of claim 4, in case the barrier layer containing at least one kind of compound which consists of at least one sort or two sorts or more of elements out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on a base material by the

plasma-CVD method is formed using the gas which has an organosilicon compound, oxygen, or oxidizing power at least, the manufacture approach of the plastic envelope characterized by being in the middle of membrane formation, and stopping supply of an organosilicon compound is offered.

[0027] In invention of claim 5, the gas which has an organosilicon compound, oxygen, or oxidizing power at least is used. On a base material by the plasma-CVD method A silicon oxide, In case the barrier layer which contains at least one kind of compound which consists of at least one sort or two sorts or more of elements out of carbon, hydrogen, silicon, and oxygen is formed, it is about supply of an organosilicon compound in the middle of membrane formation. A stop, The manufacture approach of the plastic envelope characterized by starting supply again is offered.

[0028] In invention of claim 6, the gas which has an organosilicon compound, oxygen, or oxidizing power at least is used. On a base material by the plasma-CVD method A silicon oxide, In case the barrier layer which contains at least one kind of compound which consists of at least one sort or two sorts or more of elements out of carbon, hydrogen, silicon, and oxygen is formed, it is about supply of an organosilicon compound in the middle of membrane formation. A stop, The manufacture approach of the plastic envelope characterized by repeating starting supply again is offered.

[0029] In invention of claim 7, the gas which has an organosilicon compound, oxygen, or oxidizing power at least is used. On a base material by the plasma-CVD method A silicon oxide, Carbon, hydrogen, That both the flow rates of the gas which has the flow rate and the oxygen, or the oxidizing power of an organosilicon compound in case the barrier layer which contains at least one kind of compound which consists of at least one sort or two sorts or more of elements out of silicon and oxygen is formed change The manufacture approach of the plastic envelope by which it is characterized is offered.

[0030] In invention of claim 8, the manufacture approach of the plastic envelope characterized by preparing which barrier layer of claims 1-7 in a bottle inner surface is offered.

[0031] In invention of claim 9, the plastic envelope characterized by having the plasma-CVD barrier layer in which the concentration containing at least one kind of compound which consists of at least one sort or two sorts or more of elements of an organosilicon compound changes out of a silicon oxide, carbon, hydrogen and silicon, and oxygen on one side at least is offered.

[0032] In invention of claim 10, the plastic envelope according to claim 9 characterized by decreasing while the concentration of an organosilicon compound

forms membranes is offered.

[0033] In invention of claim 11, while the concentration of an organosilicon compound forms membranes, the plastic envelope according to claim 9 characterized by repeating reduction and an increment is offered.

[0034] In both invention of claim 12, the plastic envelope according to claim 9 characterized by the concentration and the oxygen density of an organosilicon compound changing in the thickness direction is offered.

[0035] In invention of claim 13, the plastic envelope characterized by preparing which barrier layer of claims 9–12 in a bottle inner surface is offered.

[0036] The organosilicon compound which constitutes a silicon oxide layer can be chosen from 1, 1, 3, 3, – tetramethyl disiloxane, hexa methyl disiloxane, a vinyl trimethyl silane, methyl trimetoxysilane, a hexa methyl disilane, methylsilane, dimethylsilane, a trimethyl silane, a diethylsilane propyl silane, phenylsilane, vinyltriethoxysilane, vinyltrimetoxysilane, a tetramethoxy silane, a tetra–ethoxy silane, phenyltrimethoxysilane, methyl triethoxysilane, octamethylcyclotetrasiloxane, etc.

[0037] 1, 1, 3, 3, – tetramethyl disiloxane, hexa methyl disiloxane, and octamethylcyclotetrasiloxane are especially desirable.

[0038] However, it is not limited to these and an amino silane, a silazane, etc. are used.

[0039] The above–mentioned organosilicon compound which is a liquid is made to evaporate, nitrogen, fluoridation carbon, etc. are added to the material gas which mixed the helium and/or the argon which are inert gas to the gas (for example, N2O and CO2 grade) which has oxygen or oxidizing power, mixed gas, or the above–mentioned mixed gas, or this, it introduces into the plasma chemistry–gaseous–phase vacuum evaporationo machine with which the plastic envelope is installed, and all form the silicon oxide layer of 30 to 5000 A thickness. The thickness of the field of barrier nature and flexibility to 100 to 500 A is desirably desirable.

[0040]

[Embodiment of the Invention] An example is shown below using drawing. As shown in drawing 2 , a container is set in the external electrode 2 which covers a plastic envelope 1, and the gas installation tubing 3 and the exhaust port 4 used as a ground 5 are set. Next, as shown in drawing 3 , the inside and outside of a bottle are lengthened to a vacuum using a vacuum pump. By carrying out the seal of approval of the high frequency for the gas which has an organosilicon compound and oxidizing power to a sink and an external electrode from the gas installation tubing 3, the plastic envelope 1 interior is made to generate the plasma, and membranes are formed inside.

In this case, the concentration of gas is changed.

[0041] The object which finally shows a plastic envelope 1 to ejection and drawing 1 from the external electrode 2 was done.

[0042] Although membranes are formed to a plastic envelope by the above approaches, one-sheet structure or the combination of two or more sheets shall be sufficient as an electrode. Moreover, the carbon content in the film can be adjusted by changing the mixing ratio of the organosilicon compound to introduce and the gas which has oxidizing power and time amount, and a RF output.

[0043]

[Example] (Preliminary experiment) The pressure in the chamber at the time of passing the gas of hexa methyl disiloxane (HMDSO) and each oxygen is shown. The pressure at the time of dividing material gas into an organosilicon compound (1) and oxygen (2), and supplying it as the pressure when not performing HMDSO concentration change as the initial pressure in the case of performing HMDSO concentration change as conditions 1 and conditions 2 and conditions 3, is also shown. measurement of a pressure -- Pirani-vacuum-gauge PT-DB1 made from large ****** -- using -- a vacuum pump -- the product made from EDWARDS -- rotary-pump E2M-18 and the product made from ULVAC -- mechanical-booster-pump MBS-030 were used.

[0044] moreover, the conditions 2 -- an exhaust air system -- the product made from ULVAC -- the object which added cryopump U10PU is shown in conditions 4.

[0045] (Example 1) The processing time until it becomes amount of oxygen transparency 0.020 cc/pkg/day and 0.030 or less g/pkg/day of the amounts of steam transparency is shown.

[0046] The processing time when not performing HMDSO concentration change in HMDSO1.0sccm and oxygen 100sccm as an example 1 of a comparison, It is HMDSO as an example 2 of a comparison. The processing time when not performing HMDSO concentration change in 1.0sccm and oxygen 20sccm, A cryopump is added to an exhaust air system as the processing time at the time of dividing material gas into an organosilicon compound and oxygen, and supplying it as an example 3 of a comparison, and an example 4 of a comparison, and the processing time when not performing HMDSO concentration change in HMDSO1.0sccm and oxygen 100sccm is also shown.

[0047] Moreover, 0.100 cc/pkg/day and the amount of steam transparency of the amount of oxygen transparency of an unsettled PET container were 0.070 g/pkg/day.

[0048] About oxygen transmittance, if it was in steam transmittance just by OXTRAN of MOCON, it measured by PERMATRAN of MOCON.

[0049]

[A table 1]

	HMDSO 流量 (sccm)	酸素流量 (sccm)	圧力 (Torr)
条件 1	1.0	20	5.0×10^{-1}
条件 2	1.0	100	1.1×10^{0}
条件 3－1	10.0	0	7.9×10^{-1}
条件 3－2	0	20	2.9×10^{-1}
条件 4	1.0	100	1.0×10^{-2}

[0050]

[A table 2]

	成膜時間 (sec)
実施例	40
比較例 1	－
比較例 2	－
比較例 3	70
比較例 4	30

[0051] By changing HMDSO concentration, as shown above, membrane formation time amount can be shortened rather than it performs oxygen after treatment after HMDSO membrane formation. Moreover, about the example 1 of a comparison, and the example 2 of a comparison, the object in which predetermined gas barrier nature is shown was not able to be created.

[0052]

[Effect of the Invention] As explained in full detail above, according to this invention, a plastic envelope with high gas barrier nature can be created in a short time, without applying a burden to an exhaust air system.

[Translation done.]